

THE CLAIMS

What Is Claimed Is:

1. An electrode assembly for analyzing a sample metal electroplating solution, comprising a measuring electrode and at least one of (1) an *in situ* cleaning mechanism, (2) a nucleation and metal growth optimization mechanism, and (3) a voltage limiting mechanism,

said *in situ* cleaning mechanism comprising an auxiliary electrode and an auxiliary current source connected to said auxiliary electrode, wherein the measuring electrode is detachably connectable to said auxiliary current source, so that when both the measuring electrode and the auxiliary electrode are immersed in a sample metal electroplating solution or an electrolytic cleaning solution, the auxiliary current source applies a cycling electric current to the measuring electrode and the auxiliary electrode through said sample metal electroplating solution or electrolytic cleaning solution, for *in situ* cleaning and depassivating the measuring electrode;

said nucleation and metal growth optimization mechanism comprising a rotation speed controller, which is connected to the measuring electrode for rotating the measuring electrode at various rotation speeds during a metal plating/analyzing cycle, wherein during an initial nucleation stage, said rotation speed controller effectuates rotation of the measuring electrode at a first predetermined speed, wherein after said initial nucleation stage, said rotation speed controller effectuates rotation of the measuring electrode at a second predetermined speed that is substantially higher than the first predetermined speed, and wherein said rotation speed controller sends an output signal for initiation of a

subsequent metal growth stage when the rotation of the measuring electrode at said second predetermined speed stabilizes; and

said voltage limiting mechanism comprising a voltage controller for monitoring electropotential at a surface of the measuring electrode and for applying an opposite electric current to the measuring electrode when the electropotential exceeds a predetermined value, so that said electropotential is maintained at not more than said predetermined value during various stages of a metal plating/analyzing cycle.

2. The electrode assembly of claim 1, comprising said *in situ* cleaning mechanism.
3. The electrode assembly of claim 2, wherein both the measuring electrode and the auxiliary electrode are immersed in an electrolytic cleaning solution comprising sulfuric acid and optionally potassium sulfate, and wherein the auxiliary current source applies a cycling electric current to the measuring electrode and the auxiliary electrode through said electrolytic cleaning solution, for *in situ* cleaning and depassivating the measuring electrode.
4. The electrode assembly of claim 3, wherein said electrolytic cleaning solution is substantially free of copper sulfate and organic additives.
5. The electrode assembly of claim 3, wherein said electrolytic cleaning solution comprises sulfuric acid at a concentration in a range of from about 0.1M to about 1M.
6. The electrode assembly of claim 5, wherein said electrolytic cleaning solution further comprises potassium sulfate at a concentration in a range of from about 0.1M to about 1M.
7. The electrode assembly of claim 3, wherein said electrolytic cleaning solution comprises sulfuric acid at a concentration in a range of from about 0.1M to about 0.3M.

8. The electrode assembly of claim 7, wherein said electrolytic cleaning solution further comprises potassium sulfate at a concentration in a range of from about 0.3M to about 0.5M.
9. The electrode assembly of claim 2, wherein the cycling electric current applied by said auxiliary current source is characterized by a current cycling range of from about $-10\text{mA}/\text{cm}^2$ to about $10\text{mA}/\text{cm}^2$, a cycling rate of from about 0.5mA/second to about 5mA/second, and a cycling duration of at least 10 cycles.
10. The electrode assembly of claim 2, wherein the measuring electrode, the auxiliary electrode, and the auxiliary current source are integrated into a unitary module.
11. The electrode assembly of claim 2, wherein said electric current cycles from about $-8\text{mA}/\text{cm}^2$ to about $8\text{mA}/\text{cm}^2$.
12. The electrode assembly of claim 2, wherein said electric current cycles from about $-6\text{mA}/\text{cm}^2$ to about $6\text{mA}/\text{cm}^2$.
13. The electrode assembly of claim 2, wherein said electric current has a cycling rate in the range of from about 1mA/second to about 3mA/second.
14. The electrode assembly of claim 2, wherein said electric current has a cycling rate of about 2mA/second.
15. The electrode assembly of claim 2, wherein said cycling electric current is provided for at least 15 cycles.
16. The electrode assembly of claim 2, wherein said cycling electric current is provided for at least 20 cycles.

17. The electrode assembly of claim 2, wherein said cycling electric current is provided for at least 30 cycles.
18. The electrode assembly of claim 1, comprising said nucleation and metal growth optimization mechanism, wherein the first predetermined speed is in a range of from about 0 to about 10 rpm, and wherein the second predetermined speed is in a range of from about 300 to about 2400 rpm.
19. The electrode assembly of claim 18, wherein the first predetermined speed is in a range of from about 0 to about 5 rpm, and wherein the second predetermined speed is in a range of from about 500 to about 1250 rpm.
20. The electrode assembly of claim 1, comprising said voltage limiting mechanism, wherein said voltage controller comprises an analog feedback circuit connected with said measuring electrode.
21. The electrode assembly of claim 20, wherein said predetermined value is within a range of from about 0.7V to about 0.8V.
22. A method for *in situ* cleaning and depassivating a measuring electrode, comprising the steps of:
 - (a) providing an electrode assembly as in claim 1, wherein said electrode assembly comprises the *in situ* cleaning mechanism;
 - (b) detachably connecting the measuring electrode to the auxiliary current source;
 - (c) immersing both the measuring electrode and the auxiliary electrode in a sample metal plating solution or an electrolytic cleaning solution;

- (d) using said auxiliary current source to apply a cycling electric current to the measuring electrode and the auxiliary electrode through said sample metal plating solution or electrolytic cleaning solution, for a sufficient period of time for *in situ* cleaning and depassivating the measuring electrode; and
- (e) optionally, repeating steps (b)-(d) before each analytical measurement cycle.
23. The method of claim 22, wherein both the measuring electrode and the auxiliary electrode are immersed in an electrolytic cleaning solution comprising sulfuric acid and optionally potassium sulfate, and wherein the auxiliary current source applies a cycling electric current to the measuring electrode and the auxiliary electrode through said electrolytic cleaning solution, for *in situ* cleaning and depassivating the measuring electrode.
24. The method of claim 23, wherein said electrolytic cleaning solution is substantially free of copper sulfate and organic additives.
25. The method of claim 23, wherein said electrolytic cleaning solution comprises sulfuric acid at a concentration in a range of from about 0.1M to about 1M.
26. The method of claim 25, wherein said electrolytic cleaning solution further comprises potassium sulfate at a concentration in a range of from about 0.1M to about 1M.
27. The method of claim 23, wherein said electrolytic cleaning solution comprises sulfuric acid at a concentration in a range of from about 0.1M to about 0.3M.
28. The method of claim 27, wherein said electrolytic cleaning solution further comprises potassium sulfate at a concentration in a range of from about 0.3M to about 0.5M.

29. The method of claim 22, wherein the cycling electric current applied by said auxiliary current source is characterized by a current cycling range of from about $-10\text{mA}/\text{cm}^2$ to about $10\text{mA}/\text{cm}^2$, a cycling rate of from about $0.5\text{mA}/\text{second}$ to about $5\text{mA}/\text{second}$, and a cycling duration of at least 10 cycles.
30. The method of claim 29, wherein said electric current cycles from about $-8\text{mA}/\text{cm}^2$ to about $8\text{mA}/\text{cm}^2$.
31. The method of claim 29, wherein said electric current cycles from about $-6\text{mA}/\text{cm}^2$ to about $6\text{mA}/\text{cm}^2$.
32. The method of claim 29, wherein said electric current has a cycling rate in the range of from about $1\text{mA}/\text{second}$ to about $3\text{mA}/\text{second}$.
33. The method of claim 29, wherein said electric current has a cycling rate of about $2\text{mA}/\text{second}$.
34. The method of claim 29, wherein said cycling electric current is provided for at least 15 cycles.
35. The method of claim 29, wherein said cycling electric current is provided for at least 20 cycles.
36. The method of claim 29, wherein said cycling electric current is provided for at least 30 cycles.

37. A method for optimizing formation of metal nucleation sites and enhancing uniformity of metal film plated on a measuring electrode during a metal plating/analyzing cycle, comprising the steps of:
- (a) providing an electrode assembly as in claim 1, wherein said electrode assembly comprises the nucleation and metal growth optimization mechanism;
 - (b) immersing said measuring electrode in a sample metal electroplating solution;
 - (c) commencing the initial nucleation stage of the metal plating/analyzing cycle, during which the rotation speed controller rotates the measuring electrode at a first predetermined speed;
 - (d) subsequently, using the rotation speed controller to rotate the measuring electrode at a second predetermined speed that is substantially higher than the first predetermined speed;
 - (e) after the rotation of the measuring electrode stabilizes at said second predetermined speed, using the rotation speed controller to send an output signal for initiation of a subsequent metal growth stage; and
 - (f) measuring electropotential of the measuring electrode during the metal growth stage, for determination of concentration of a specific metal additive in said sample electroplating solution.
38. The method of claim 37, wherein the first predetermined speed is in a range of from about 0 to about 10 rpm, and wherein the second predetermined speed is in a range of from about 300 to about 2400 rpm.

39. The method of claim 37, wherein the first predetermined speed is in a range of from about 0 to about 5 rpm, and wherein the second predetermined speed is in a range of from about 500 to about 1250 rpm.
40. A method for protecting a measuring electrode against surface rearrangement during a metal plating/analyzing cycle, comprising the steps of:
- (a) providing an electrode assembly as in claim 1, wherein said electrode assembly comprises the voltage limiting mechanism;
 - (b) using said voltage limiting mechanism to continuously monitor electropotential of the measuring electrode during said metal plating/analyzing cycle; and
 - (c) when the electropotential of the measuring electrode exceeds a predetermined value, using said voltage limiting mechanism to apply an opposite electrode current to the measuring electrode, for maintaining the electropotential of such measuring electrode at not more than said predetermined value during the metal plating/analyzing cycle.
41. The method of claim 40, wherein said voltage controller comprises an analog feedback circuit connected with said measuring electrode.
42. The method of claim 40, wherein said predetermined value is within the range of from about 0.7V to about 0.8V.